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(11) Publication number:

0 095 975
A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 83401041.5

(51) Int. Cl.³: C 10 L 1/22, C 09 B 1/32

(22) Date of filing: 25.05.83

(30) Priority: 27.05.82 IT 2150682

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(43) Date of publication of application: 07.12.83
Bulletin 83/49

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(84) Designated Contracting States: BE DE FR GB NL

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(54) Concentrated solutions of 1,4-dialkyl-arylamino-anthraquinone dyestuffs for the colouring of petroleum products.

(55) The invention relates to concentrated solutions of dye-stuffs for petroleum products and organic solvents, comprising an organic diluent phase and from 30 to 50% by weight of one or more 1,4-dialkyl-arylamino-anthraquinone dyes, wherein the two alkyl radicals, equal to or different from each other, contain from 8 to 20 carbon atoms and are obtained by reacting quinizarin or leucoquinizarin or mixtures thereof with one or more para-alkylanilines.

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CONCENTRATED SOLUTIONS OF 1,4-DIALKYL-ARYLAMINO-ANTHRAQUINONE
DYESTUFFS FOR THE COLOURING OF PETROLEUM PRODUCTS

The present invention refers to concentrated solutions of 1,4-dialkyl-arylarnino-anthraquinone dyestuffs (herein-after called "dyes") suitable for the coloring of petroleum products and industrial organic solvents

The colouring of the industrial organic solvents and of the petroleum products such as, for instance gasoline, kerosene, gas oil, is carried out in order to render them identifiable, and thus make difficult the possible taxevasions, which can result from utilizing said products for purpose that differ from the ones for which they are taxed. The colouring material, in order that it may be used in the colouring of fuels, must satisfy various requirements, i.e. among other:

- 1) possess a high dyeing power;
- 15 2) have a sufficient solubility in the solvents and in the fuels whether or not antiknock agents have been added;
- 3) have a high diffusion index;
- 4) contain little or no by-product insoluble in fuels;
- 5) leave only a minimum deposit of sludge in the engines;
- 20 6) have a proper fastness to light during storage;
- 7) be compatible with additives and not cause difficulties during combustion;
- 8) be brittle but not powderous in the solid form;
- 9) be sufficiently fluid to be solubilized in organic solvents, if it
- 25 is used in the form of a concentrated solution.

The use in the form of concentrated solution allows considerable advantages with respect to powdery products:

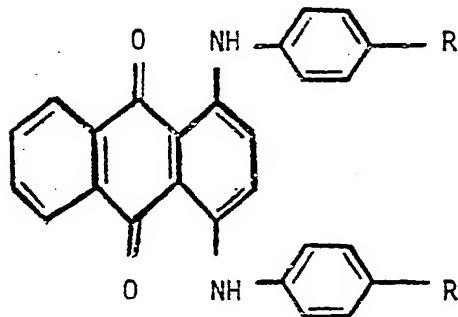
- a) easiness of use,
- b) rapidity of dosage;
- 30 c) high diffusion coefficient;
- d) absence of powders.

All these characteristics, although necessary, are, however, not sufficient for the choice of the suitable dye, since the dye must primarily be extractable with difficulty from the system in which it is dissolved.

Anthraquinonic dyes, employable for the colouring of the petroleum products are known from the literature, such as, for instance, U.S. patent 2,211,943; U.S. patent 2,925,333; U.S. patent 3,164,499, however, they hardly succeed in satisfying the above listed requisites and in particular present on the one hand a limited solubility in the organic solvent and the other hand non-extractability characteristics, that are inadequate in many cases.

The anthraquinonic dyes for fuels having the following structures, are particularly known in the art:

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where R = H, CH₂

20

(Solvent Blue 76, Solvent Green 3/C.I. 61565)

(I)

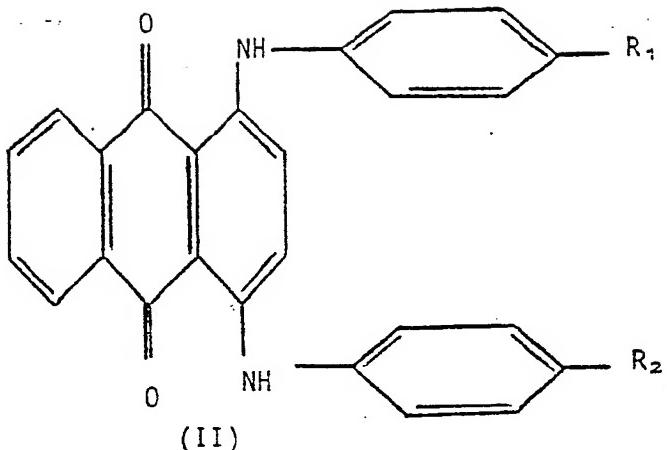
However, the solubility of these dyes in the various solvents is very limited, chiefly with regard to the obtention of concentrated solutions, which should also be sufficiently stable at low temperatures; therefore such dyes only find use as powders.

Furthermore, they are easily extractable from the system. Now it has been found that it is possible to colour permanently petroleum products and industrial organic solvents, over coming the above drawbacks that are shown be the known anthraquinonic dyes, by using concentrated solutions of anthraquinonic dyes comprising, in particular, alkyl-arylamino groups.

Therefore, the present invention concerns concentrated colouring solutions of blue-green tone for petroleum products and organic solvents, consisting of a diluent organic phase and of from 30 to 50% by weight of an anthraquinonic compound or of a mixture of anthraquinonic compounds having the general formula:

5

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where in:

R_1 and R_2 , equal to or different from each other, represent alkyl radicals having from 8 to 20 carbon atoms.

15 The diluent organic phase consists of one or more organic solvents such as, for instance, alpha-chloronaphthalene, alpha and beta methyl-naphthalene, alpha-bromonaphthalene, dichlorobenzene, trichlorobenzene, xylene, toluene, nitrobenzene, para-nonylphenol and aliphatic alcohols.

In fact, it has been found that the anthraquinonic dyes of general
20 formula II, according to the invention, besides answering the various requisites that dyes for fuels must meet, present unexpected characteristics of high solubility in the above cited organic solvents, so that it is possible to employ said dyes in the form of concentrated solutions, which are also sufficiently stable at low temperatures.

25 Furthermore, it has been found that the dyes of formula II, according to the invention, present surprising characteristics of difficult extractability from the fuels and in particular they appear remarkably less extractable than homologous known dyes of formula I.

In practice, solutions in fuels of the dyes of the invention of
30 formula II, have shown, when treated with quantities of silica gel ranging from 120 to 25 gr. per litre fuel, an extractability of 16 to 50% lower than that, showed by analogous solutions in fuels of the dyes of formula I. The concentrated solutions of dyes, according to the invention, are prepared by reacting quinizarin or leucoquinizarin or mixtures thereof and
35 one or more para-alkylanilines in the presence of or after subsequent addition of the above mentioned organic solvents.

The use of a mixture of para-alkylanilines in the synthesis of the dyes allows the formation of a mixture of dyes of formula II, comprising both symmetrical derivatives (R_1 equal to R_2) and asymmetrical derivatives

(R₁ different from R₂).

The dye mixture thus obtained shows a higher solubility in the organic solvents, with respect to the dye obtained from a single para-alkylaniline.

5 The synergic solubilizing effect of the dye mixture is such that said mixtures appear in an oily or semioily form, which allows to obtain dye solutions having a high concentration in the above mentioned organic solvents. Concentrated dye solutions, ready - to - use and particularly advantageous are prepared by condensing the hydroxyanthraquinones with
10 the mixture of chosen para-alkylanilines, ending with the oxidation "in situ" of the still present leucoderivatives by means of nitrobenzene or of organic compounds of similar characteristics and with the dilution of the reaction bulk with one or more organic solvents, followed by an aqueous extraction of the present inorganic salts and a final anydification.
15 A further advantage of the dyes of the invention, with respect to the known dyes of formula I, resides in the lower toxicity of the para-alkylanilines having an aliphatic chain with a high number of atom carbon (8 to 20), used in the synthesis of said dyes of formula II, with respect to the aniline or the para-toluidine used in the sunthesis of the dyes of
20 formula I.

The following examples are given to better illustrate the invention, without limiting, however, its scope.

EXAMPLE N° 1

0.1 moles of quinizarin, 0.05 moles of leuco-quinizarin, 0.675 moles
25 of boric acid, 0.45 moles of n-dodecylaniline, 75 g of isobutanol were
heated to boiling point (105°C) during several hours.

The whole was cooled to room temperature.

100 g of xylene were added.

Several washings were carried out by using 100 g of water at a time;
30 after decantation, the aqueous layer was separed.

250 g of a blue color concentrated solution containing 40% by weight of dye was obtained.

EXAMPLE N° 2

0.1 moles of quinizarin, 0.05 moles of leuco-quinizarin, 0.675 moles
35 of boric acid, 0.60 moles of a mixture (C₁₀ - C₁₈) of para-alkylanilines
were heated to 165°C for 10 hours.

The whole was cooled to room temperature.

60 g of mixture of toluene/p-nonylphenol were added.

Some washings were carried out by using 100 g of water at a time; after decantation, the aqueous layer was separated.

300g of a mixture of blue dyes in concentrated solution containing 30% of dyes was obtained..

5 EXAMPLE N° 3

0.15 moles of leuco-quinizarin, 0.675 moles of boric acid, 0.45 moles of n-dodecylaniline, 75 g of isobutanol were heated to boiling temperature (105°C) for 10 hours. 0.075 moles of nitrobenzene were added and the temperature was kept at 110°C for further 4 hours.

10 The whole was cooled to room temperature.

100 g of a mixture of alpha/beta-methylnaphthalene were added. Several washings were carried out by using 100 g of water at a time; after one decantation the aqueous layer was separated.

250 g of a blue color concentrated solution, containing 40% of dye 15 was obtained.

EXAMPLE N° 4

0.1 moles of quinizarin, 0.05 moles of leuco-quinizarin, 0.675 moles of boric acid, 0.45 moles of a mixture ($C_{10} - C_{18}$) of para-alkylanilines, 75 g of isobutanol were heated to boiling temperature (105°C) for 10 hours.

20 The whole was cooled to room temperature.

140 g of xylene were added.

Several washings were carried out by using 100 g of water at a time; after decantations the aqueous layer was separated.

300 g of a mixture of blue color concentrated solution containing 25 30% of dyes were obtained.

EXAMPLE N° 5

0.15 moles of leuco-quinizarin, 0.675 moles of boric acid, 0.45 moles of a mixture ($C_{10} - C_{18}$) of alkylanilines, 75 g of isobutanol were heated to boiling temperature (105°C) for 10 hours.

30 0.075 moles of nitrobenzene were added and the temperature was kept at 110°C for further 4 hours.

The whole was cooled to room temperature.

50 g of a mixture of alpha-/beta-methylnaphthalene were added.

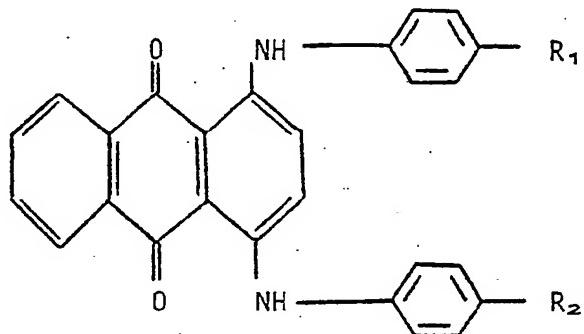
Several washings were carried out by using 100 g of water at a time; 35 after decantation the aqueous layer was separated.

200 g of a mixture of blue color concentrated solution containing 50% of dyes were obtained.

C L A I M S

1.- Concentrated colouring solutions of blue-green tone for liquid petroleum products and organic solvents consisting of an organic diluent phase and of from 30 to 50% by weight of an anthraquinonic compound or of
 5 a mixture of anthraquinonic compounds having general formula:

10



15 where in:

R₁ and R₂, equal to or different from each other, represent alkyl radicals having from 8 to 20 carbon atoms, obtained by reacting quinazarin or leuco-quinizarin or mixtures thereof with one or more para-alkylanilines.

20 2.- Concentrated solutions, according to claim 1, wherein the organic diluent phase consists of one or more solvents selected from the group consisting of alpha- and beta-methylnaphthalene, para-nonylphenol, nitrobenzene, toluene, xylene, aliphatic alcohols.

25 3.- Petroleum products and solvents, when coloured with colouring concentrated solutions, as claimed in the herein above preceding claims.

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European Patent
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EUROPEAN SEARCH REPORT

Application number

EP 83 40 1041

DOCUMENTS CONSIDERED TO BE RELEVANT		Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 5)			
Category	Citation of document with indication, where appropriate, of relevant passages					
A	DE-A-3 019 136 (ACNA SpA) * Claims 1,5,6 *	1-3	C 10 L 1/22 C 09 B 1/32			
A	GB-A-1 108 981 (WILLIAMS LTD.) * Claims 1-9 *	1-3				
A	GB-A-1 126 704 (ALLIED CHEMICAL) * Claims 1,9,10,15 *	1-3				

			TECHNICAL FIELDS SEARCHED (Int. Cl. 5)			
			C 09 B C 10 L			
<p>The present search report has been drawn up for all claims</p> <table border="1"> <tr> <td>Place of search THE HAGUE</td> <td>Date of completion of the search 30-08-1983</td> <td>Examiner ROTSAERT L.D.C.</td> </tr> </table> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>				Place of search THE HAGUE	Date of completion of the search 30-08-1983	Examiner ROTSAERT L.D.C.
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